

## The First 3-Methanediyl-1,3,5,6-tetraphosphabicyclo[3.1.0]hex-2-ene. Evidence for a [3 + 2] Cycloaddition of a 2,4,5,6-Tetraphosphahepta-1,3,6-triene

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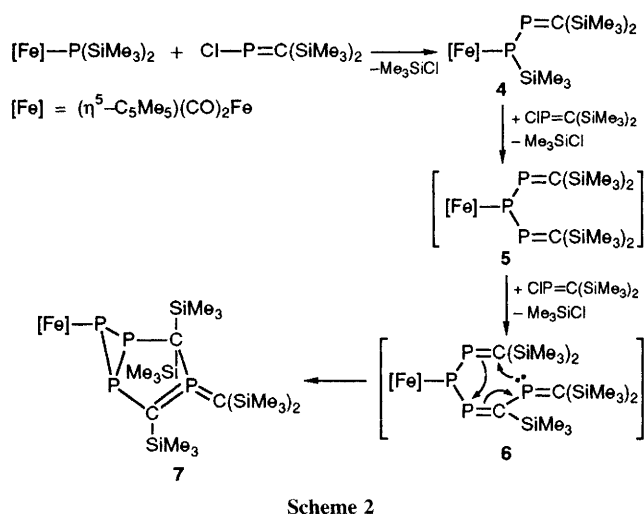
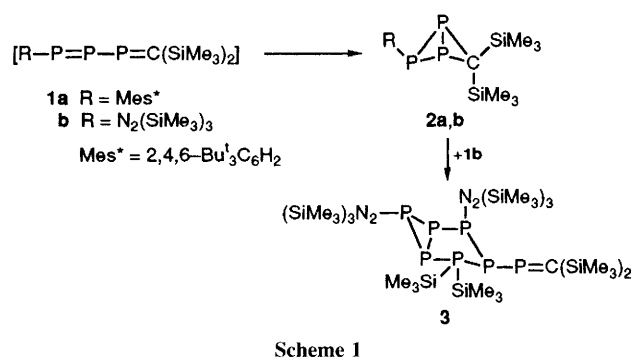
Reaction of  $(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2\text{FeP}(\text{SiMe}_3)_2$  with three equivalents of  $\text{Cl-P}=\text{C}(\text{SiMe}_3)_2$  affords the first 3-methanediyl-1,3,5,6-tetraphosphabicyclo[3.1.0]hex-2-ene **7**, the molecular structure of which has been determined by X-ray analysis.

Conjugated and non-conjugated phosphacarbaoligoenes with  $\text{P}=\text{C}$ - and  $\text{P}=\text{P}$ - functionalities are only stable in the presence of very bulky substituents.<sup>1</sup> Otherwise they tend to undergo intramolecular cyclization processes to produce interesting bicyclic organophosphorus systems such as **2** or **3**.<sup>2</sup>

Metallated phosphacarbaoligoenes of the type **4** display an interesting coordination chemistry with the generation of novel ligand systems,<sup>3</sup> which motivated us to synthesize the metallated 2,3,4-triphosphapenta-1,4-diene **5**. To our surprise we obtained the bicyclic bismethylenephosphorane **7** instead of **5**.

Reaction of  $(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2\text{FeP}(\text{SiMe}_3)_2$ <sup>4</sup> with two equivalents of chlorobis(trimethylsilyl)methylenephosphane<sup>5</sup> in tetrahydrofuran (THF) at 20 °C lead to the formation of the diphosphaallyl complex  $(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2\text{FeP}(\text{SiMe}_3)\text{P}=\text{C}(\text{SiMe}_3)_2$  **4** and minor amounts of the red crystalline **7**. In the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of the reaction mixture there was no evidence for the 2,3,4-triphosphapenta-1,4-diene **5**. Previously Appel described the synthesis of an analogue of **5** the compound  $\text{Bu}^t\text{P}[\text{P}=\text{C}(\text{Ph})(\text{SiMe}_3)]_2$ , which, however, decomposed during the attempted isolation.<sup>6</sup>

The yield of **7** could be optimized to 27% when  $(\eta^5\text{-$



C<sub>5</sub>Me<sub>5</sub>(CO)<sub>2</sub>FeP(SiMe<sub>3</sub>)<sub>2</sub> was treated with a threefold excess of the chloromethylenephosphane. Separation of **7** was achieved by removing the solvent and crystallization of the residue from diethyl ether at -30 °C. The constitution of **7** as a representative of the unknown 3-methanediyl-1,3,5,6-tetra-phosphabicyclo[3.1.0]hex-2-ene system was shown by electron impact mass spectrometry (70 eV, M<sup>+</sup> *m/z* 772) as well as by <sup>31</sup>P NMR.†

The bicyclic structure of **7** (Fig. 1) is further confirmed by X-ray crystal determination.‡

† Selected spectroscopic data for **7**: <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>): δ = -174.0 (ddd, <sup>1</sup>J<sub>31</sub> 218, <sup>1</sup>J<sub>32</sub> 179, <sup>2</sup>J<sub>34</sub> 15 Hz, P3), -144.7 (ddd, <sup>1</sup>J<sub>21</sub> 193, <sup>1</sup>J<sub>23</sub> 179, <sup>2</sup>J<sub>24</sub> 32 Hz, P2), -49.7 (ddd, <sup>1</sup>J<sub>13</sub> 218, <sup>1</sup>J<sub>12</sub> 193, <sup>3</sup>J<sub>14</sub> 15 Hz, P1), 171.9 (dt, <sup>2</sup>J<sub>43</sub> 32, <sup>2</sup>J<sub>43</sub> <sup>3</sup>J<sub>41</sub> 15 Hz, P4); <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ = 0.42 (d, *J*<sub>PH</sub> 2.6 Hz, 9H, SiMe<sub>3</sub>), 0.46 (s, 9H, SiMe<sub>3</sub>), 0.52 (s, 9H, SiMe<sub>3</sub>), 0.68 (d, *J*<sub>PH</sub> 1.4 Hz, 9H, SiMe<sub>3</sub>), 0.72 (m, 9H, SiMe<sub>3</sub>), 1.45 (d, *J*<sub>PH</sub> 0.7 Hz, 15 H, C<sub>5</sub>Me<sub>5</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>): δ = 3.19 (m, SiMe<sub>3</sub>), 5.02 (m, SiMe<sub>3</sub>), 6.95 (m, SiMe<sub>3</sub>), 9.42 [dd, *J*<sub>PC</sub> 6.0, 1.0 Hz, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>], 39.65 [ddd, *J*<sub>PC</sub> 98.3, 35.1, 8.5 Hz, P<sub>2</sub>C(SiMe<sub>3</sub>)], 56.22 [dt, *J*<sub>PC</sub> 20.9, 4.5 Hz, P=C(SiMe<sub>3</sub>)<sub>2</sub>], 96.34 [d, *J*<sub>PC</sub> 1.1 Hz, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>], 215.37 (m, CO); IR (KBr): ν/cm<sup>-1</sup> = 1990, 1947 [ν(CO)].

‡ Crystal data: C<sub>30</sub>H<sub>60</sub>FeO<sub>2</sub>P<sub>4</sub>Si<sub>5</sub>; **7**: M = 773.0, triclinic space group P1, *a* = 9.174(2), *b* = 12.136(4), *c* = 20.041(6) Å, α = 80.81(3), β = 84.89(2), γ = 74.95(2)°, V = 2124.4(11) Å<sup>3</sup>, Z = 2, λ (Mo-Kα) = 0.71073 Å, μ (Mo-Kα) = 0.665 mm<sup>-1</sup>, D<sub>c</sub> = 1.208 g cm<sup>-3</sup>. The structure was solved by direct methods and refined by full-matrix least-squares refinement to a current R<sub>w</sub> = 0.060, based on 3570 reflections with F<sub>o</sub> > 4.0σ(F<sub>o</sub>). Atomic coordinates, bond lengths, angles and displacement parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

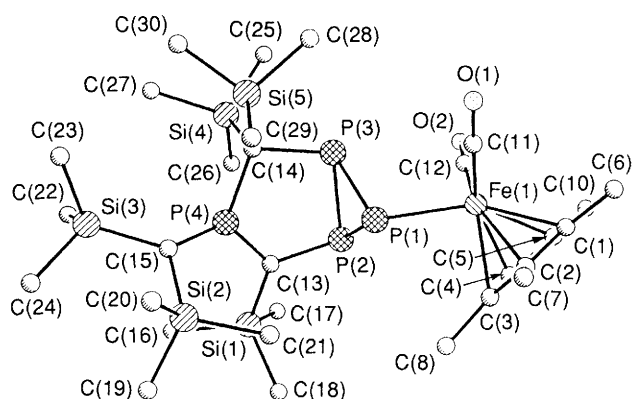


Fig. 1 View of **7** with selected bond lengths (Å) and angles (°): P(1)-P(2) 2.202(4), P(1)-P(3) 2.195(3), P(2)-P(3) 2.210(3), P(1)-Fe(1) 2.321(3), P(2)-C(13) 1.799(9), P(4)-C(13) 1.680(8), P(4)-C(14) 1.853(8), P(4)-C(15) 1.673(10), P(3)-C(14) 1.893(8), Si(1)-C(13) 1.876(8), Si(2)-C(15) 1.864(8), Si(3)-C(15) 1.853(8), Si(4)-C(14) 1.927(8), Si(5)-C(14) 1.920(8); P(1)-P(2)-P(3) 59.7(1), P(1)-P(3)-P(2) 60.0(1), P(2)-P(1)-P(3) 60.4(1), P(2)-P(3)-C(14) 102.1(3), P(3)-C(14)-P(4) 106.5(3), C(14)-P(4)-C(15) 127.7(4), C(13)-P(4)-C(14) 108.7(4), C(13)-P(4)-C(15) 123.4(4), P(2)-C(13)-P(4) 118.2(5), P(3)-P(2)-C(13) 98.1(3), P(2)-C(13)-Si(1) 114.5(5), P(4)-C(13)-Si(1) 126.5(5), P(4)-C(15)-Si(3) 127.3(5), P(4)-C(15)-Si(2) 116.9(4), Si(2)-C(15)-Si(3) 115.7(5)

The molecule exhibits the sterically favoured envelope conformation with an endocyclic P=C bond distance of 1.680(8) Å, which compares well with the exocyclic PC double bond [1.673(10) Å]. The phosphorus P(4) and both carbon atoms C(13) and C(15) are planar [ $\Sigma_{\text{bond angles}}$  359.8(4), 359.2(5) and 359.9(5)°], respectively. The planes defined by P(2)-C(13)-Si(1) and Si(2)-C(15)-Si(3) are twisted by 34.6 and 48.8° with respect to plane P(4)-C(13)-C(15). We propose that **7** is formed by an intramolecular electrocyclic reaction of transient 2,4,5,6-tetra-phosphahexa-1,3,6-triene **6**. The latter results from the condensation of the hypothetical **5** and Cl-P=C(SiMe<sub>3</sub>)<sub>2</sub>.

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